Polymerization

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Palladium(0)-Catalyzed Synthesis of Cross-Conjugated Polymers: Transformation into Linear-Conjugated Polymers through the Diels–Alder Reaction

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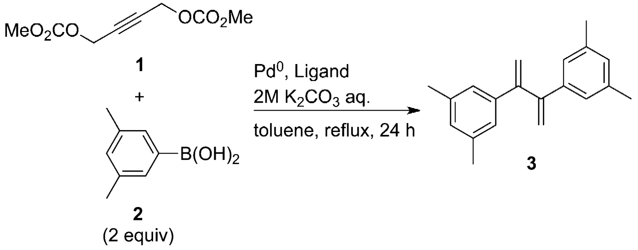
Palladium(0)-catalyzed reactions of propargylic compounds with nucleophiles have been shown to be effective for the synthesis of heterocyclic compounds,[1] allylic compounds,[2] and allenes.[3] As an application of these reactions to polymer synthesis, we have reported that the palladium(0)-catalyzed polycondensation of propargylic carbonates with bifunctional nucleophiles gives exomethylene-containing polymers.[4] Recently, a palladium(0)-catalyzed coupling reaction of propargylic bis(carbonate)s with organoboron compounds has been reported by Böhmer and Grigg, and the reaction produced diarylated dienes in moderate to good yields.[5] The results prompted us to undertake a synthetic investigation of cross-conjugated polymers by palladium(0)-catalyzed cross-coupling polymerization between a propargylic bis(carbonate) and diboron compounds. Conjugated polymers have received much attention because of their various applications such as light-emitting diodes,[6] chemical sensors,[7] and electronic devices.[8] The most studied frameworks for conjugated polymers are linearly conjugated π systems. In contrast to the conjugated polymers, cross-conjugated polymers have been less studied. However, cross-conjugated compounds have recently attracted increasing attention because of their potential for various applications.[9] For example, poly(arylene-1,1-vinylene)s are synthesized by Weber and coworkers[10] and Itami et al.[11] Cross-conjugated polymers would present new opportunities for material science.

Poly(arylene-2,3-butadienylene)s, which have sequential 1,1-vinylene groups in the monomer unit, have not been reported so far. We anticipated that cross-conjugated polymers having 2,3-butadienylene moieties in the main chain would be quite interesting because the conversion of them into conjugated polymers would easily be accomplished through reactions such as the Diels–Alder reaction. This approach would be a new protocol for the synthesis of conjugated polymers. We report herein the synthesis of new cross-conjugated polymers by palladium(0)-catalyzed cross-coupling polymerization of a propargylic bis(carbonate) with diboron compounds, and their transformation into conjugated polymers.

We first examined the palladium(0)-catalyzed reaction of the propargylic bis(carbonate) **1** with 3,5-dimethylphenyl boronic acid (**2**) as a model reaction (Table 1). The reaction of **1** with **2** was conducted using the conditions reported by Böhmer and Grigg, that is, $Pd(OAc)_2$ and PPh_3 in toluene at 65 °C.[5] The expected 2,3-diarylated-1,3-butadiene **3** was obtained as a cross-conjugated product. However, the yield was low (21 %) and the conversion of **1** was 55 %. Carbonate **1** was completely consumed when the reaction was carried out at reflux, but the yield did not increase (entry 1). Various phosphine ligands were examined for the reaction. $P(o\text{-Tolyl})_3$ was also not effective (entry 2), however, the yield of **3** significantly increased with use of 2-dicyclohexylphosphino-2,6-dimethoxybiphenyl (S-Phos; entry 3). Using 2-dicyclohexylphosphino-2,4,6-triisopropylbiphenyl (X-Phos) did not afford **3** at all (entry 4). $[Pd_2(dba)_3]\cdot CHCl_3$ was more effective than $Pd(OAc)_2$ as a palladium source, with the yield of **3** increasing up to 92 % (entry 5). A lower loading of the palladium (5 mol % of Pd) did not cause a significant decrease in the yield (entry 6). The palladium(0)-catalyzed cross-coupling reaction of **1** with 9,9-dioctylfluorene-2-boronic acid (**4**) gave the corresponding diarylated diene **5** in good yield (Scheme 1).

Table 1: Palladium(0)-catalyzed cross-coupling reaction of propargylic bis(carbonate) **1** with 3,5-dimethylphenyl boronic acid **2**.[a]



Entry	Cat. Pd	Ligand	Pd [mol %]	Yield [%][b]
1	$Pd(OAc)_2$	PPh_3	10	18
2	$Pd(OAc)_2$	$P(o\text{-Tolyl})_3$	10	27
3	$Pd(OAc)_2$	S-Phos	10	72
4	$Pd(OAc)_2$	X-Phos	10	0
5[c]	$[Pd_2(dba)_3]\cdot CHCl_3$	S-Phos	10	92
6[c]	$[Pd_2(dba)_3]\cdot CHCl_3$	S-Phos	5	84
7[c]	$[Pd_2(dba)_3]\cdot CHCl_3$	S-Phos	2	62

[a] Reaction conditions: **1** (0.5 mmol), boronic acid **3** (1.0 mmol), Pd/P (1:2), 2 M K_2CO_3 aq. (1.0 mL), toluene (2 mL), reflux, 24 h. [b] Yield of isolated product. [c] Pd/P (1:1). dba = dibenzylidene acetone.

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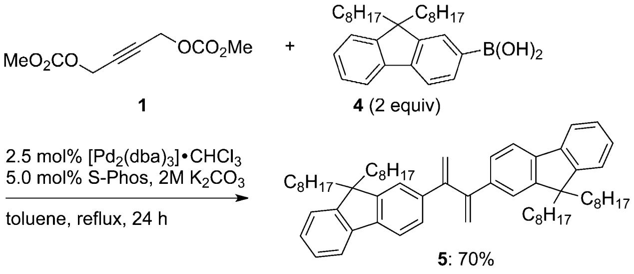
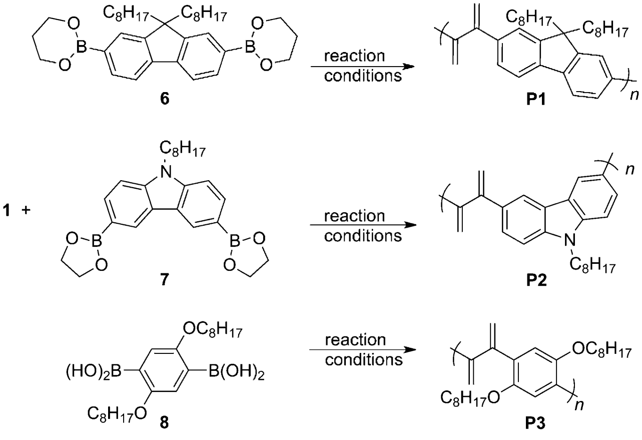


Scheme 1. Palldium(0)-catalyzed cross-coupling reaction of **1** with 9,9-dioctylfluorene-2-boronic acid (**4**).

On the basis of the results of the model reaction, we next investigated the palladium(0)-catalyzed cross-coupling polymerization of **1** with 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol ester) (**6**; Table 2). The polymerization of **1** with **6** (1 equiv) proceeded to give the corresponding cross-conjugated polymer **P1** in 54% yield, but the M_n value was rather low (entry 1). We reported that the palladium(0)-catalyzed polycondensation of bis(phenol)s with an excess of propargylic carbonates proceeded successfully to afford higher molecular weight polyethers.[4] This success resulted from because a small amount of propargyl carbonate was decomposed by the palladium catalyst used. Therefore, we tried the polymerization with **6** by using excess **1**. When 0.8 equivalents of **6** was used, the corresponding polymer **P1** was obtained quantitatively, and the M_n value increased to 7500 (entry 2). The corresponding polymer **P1** having a moderate M_n value was produced even when 0.4 equivalents of **6** were used (entry 3). *N*-Octylcarbazole-3,6-bis(ethyleneboronate) (**7**) and 2,5-dioctyloxyphenylene-1,4-diboronic acid (**8**) also gave the corresponding cross-conjugated polymers **P2** and **P3** (entries 4 and 5). The structures of the obtained polymers **P1**–**P3** were confirmed by FT/IR analysis and NMR spectroscopy. All the polymers were soluble in common organic solvents such as THF, toluene, and $CHCl_3$. The thermal stability of these polymers was investigated by thermal gravimetric analysis (TGA) under a helium atmosphere. All the polymers showed good thermal stability with 5% weight loss at temperatures (T_d) above 300°C (see Figure S1 in the Supporting Information).

To convert the cross-conjugated polymers **P1**–**P3** into conjugated polymers, the Diels–Alder reaction of **P1**–**P3** with dienophiles was explored. Among the dienophiles tested, *N*-phenyl-1,3,4-triazoline-2,5-dione (PTAD) was most reactive. The Diels–Alder reactions of each of the polymers **P1**–**P3** with PTAD (1 equiv) were carried out in THF, and were complete within a few minutes, successfully delivering the expected linear-conjugated polymers **DP1** ($M_n = 9800$, $M_w/M_n = 5.57$), **DP2** ($M_n = 3300$, $M_w/M_n = 2.39$), and **DP3** ($M_n = 6400$, $M_w/M_n = 2.56$). In contrast, the Diels–Alder reaction of the cross-conjugated product **3** with PTAD required a longer reaction time (1 h) and excess PTAD (3 equiv) to complete its transformation into the corresponding conjugated product. The representative ^1H NMR spectra of **P1** and **DP1** are shown in Figure 1. Complete consumption of **P1** was confirmed by the disappearance of the signals for the diene groups, and the appearance of signals corresponding to the methylene groups of **DP1** were observed. The FT/IR spectrum of **DP1** showed a strong absorption band at $\nu = 1779\ cm^{-1}$ and is attributed to the carbonyl group. In the ^{13}C NMR spectrum of **DP1**, the carbonyl carbon atom was observed at $\delta = 152.57$ ppm. These data support the structure

Table 2: Palladium(0)-catalyzed cross-coupling polymerization of propargylic bis(carbonate) **1** with diboron compounds **6**–**8**.[a]



Entry	Diboron compounds	Equiv.	Polymer	Yield [%][b]	M_n[c]	M_w/M_n[c]
1	**6**	1.0	**P1**	54	2700	1.68
2	**6**	0.8	**P1**	quant.	7500	4.22
3	**6**	0.4	**P1**	94	5400	3.49
4	**7**	0.8	**P2**	81	2700	2.71
5	**8**	0.8	**P3**	82	6400	2.81

[a] Reaction conditions: **1** (0.25 mmol), diboron compounds **6**–**8** (0.1–0.25 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (2.5 mol%), S-Phos (5.0 mol%), 2 M K_2CO_3 aq. (1.0 mL), toluene (2 mL), reflux, 24 h. [b] Insoluble in MeOH. Yields are based on the diboron compound. [c] Estimated by GPC (PSt).

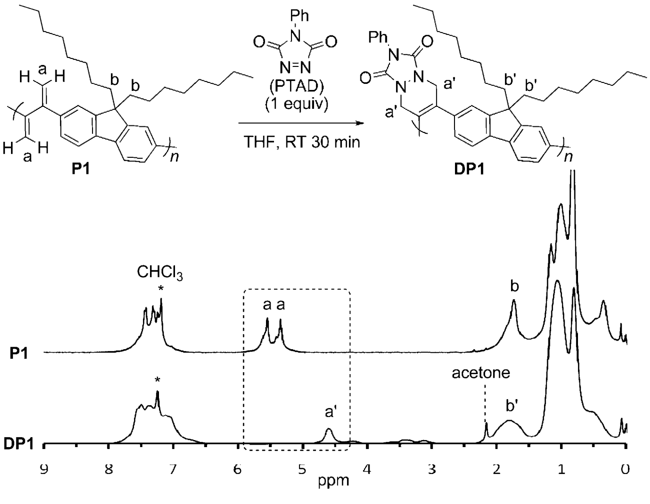


Figure 1. ^1H NMR spectra of **P1** and **DP1** in $CDCl_3$ (300 MHz). The disappearance of the signal corresponding to the diene protons (a: δ=5.34 and 5.55 ppm) of **P1** and appearance of those for the methylene protons (a′: $\delta = 4.65$ ppm) of **DP1** show the complete transformation of **P1** into **DP1** through the Diels–Alder reaction of **P1** with PTAD.

of **DP1**, and the structures of **DP2** and **DP3** were similarly confirmed. These polymers are composed of an all-*cis* conformation. Similar all-*cis* conjugated polymers were also synthesized by Suzuki–Miyaura cross-coupling polymerization of 2,3-dibromomaleimide with diboronic acids,[12] however, this procedure gave low-molecular-weight polymers, probably as a result of debromination of 2,3-dibromomaleimide.

The optical properties of the cross-conjugated polymers **P1**–**P3** and linear-conjugated polymers **DP1**–**DP3** were measured in a THF solution. The representative UV/Vis absorption and fluorescence spectra of **P1** and **DP1** are shown in Figure 2. The absorption maximum of **P1** was observed at $\lambda_{max} = 325$ nm. The conjugated polymer **DP1** exhibited a broad shoulder around $\lambda = 350$ nm along with $\lambda_{max} = 320$ nm. Polymers **P2, DP2**, **P3**, and **DP3** also showed similar behavior (see Figures S2 and S3 in the Supporting Information). These results indicate that the conjugation path of **DP1**–**DP3** was not extended along the polymer backbone. This phenomenon is probably due to interruption of the π-electron delocalization caused by the twist of the polymer backbone having an all-*cis* configuration.

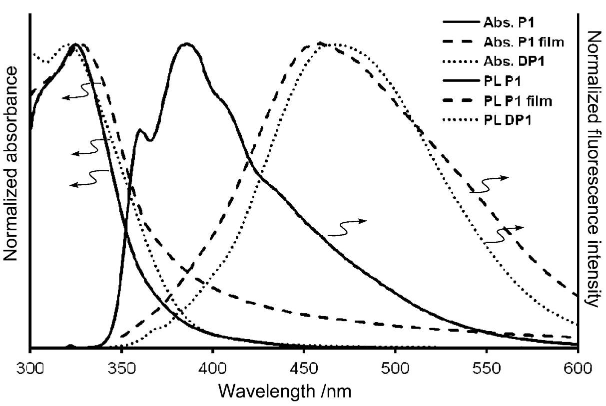


Figure 2. Normalized absorption and fluorescence spectra of **P1** (solid), **DP1** (dotted) in THF, and for the **P1** film (dashed).

The fluorescence spectra of the polymers were recorded with the excitation wavelength corresponding to the maximum absorption wavelength. The cross-conjugated polymer **P1** showed two fluorescent emission peaks at $\lambda = 361$ and 386 nm along with a shoulder around $\lambda = 440$ nm. Interestingly, a large redshift was observed in the fluorescent spectrum of the conjugated polymer **DP1** ($\lambda_{em} = 473$ nm), and the fluorescent emission changed from blue to green. The fluorescence spectra of polymer **DP2** ($\lambda = 458$ nm) and **DP3** ($\lambda = 470$ nm) also showed redshifts compared to those of the original polymer **P2** ($\lambda = 398$ nm) and **P3** ($\lambda = 413$ nm), respectively. These linear-conjugated polymers **DP1**–**DP3** showed large Stokes shifts (ca. 150 nm). There are two possible reasons for these large redshifts: 1) intramolecular charge transfer between the fluorene and the dienophile moieties or 2) energy transfer between the arylene moieties. To clarify the reason for the large Stokes shift, we next synthesized another linear-conjugated polymer, **DP4**, through a Diels–Alder reaction of **P1** with maleic anhydride in toluene at reflux for 24 hours. We anticipated that the **DP4** would show a different fluorescence spectrum if intramolecular charge transfer occurs between the fluorene and the dienophile moieties. The observed fluorescence spectrum of **DP4** was similar to that of **DP1** (see Figure S4 in the Supporting Information), thus suggesting that the fluorescence spectra of the conjugated polymers **DP1**–**DP4** were hardly affected by the dienophile moiety.

A large Stokes shift (131 nm) was observed for a **P1** film prepared by spin coating onto a glass plate (Figure 2, dashed line). **P2** and **P3** films also showed large Stokes shifts (see Figures S2 and S3 in the Supporting Information). These phenomena were similar to those of *cis*-linked conjugated polymers **DP1**–**DP4**. X-ray diffraction, as reported by van Walree et al., of 2,3-diphenyl-1,3-diene shows s-gauche to be the preferred geometry with a face-to-face arrangement of the phenyl groups in the solid state.[13] The films of **P1**–**P3** do consist mainly of the units in an s-gauche conformation. It has also been reported that multilayered chromophoric groups show large Stokes shift.[14] Therefore, the observed large Stokes shifts for **DP1**–**DP4** would be based on the energy transfer between the arylene moieties.

In conclusion, a series of new cross-conjugated polymers (**P1**–**P3**) were synthesized by palladium(0)-catalyzed cross-coupling polymerization between propargylic bis(carbonate) **1** and diboron compounds. The cross-coupling polymerization proceeded efficiently when using the $[Pd_2(dba)_3]\cdot CHCl_3$/S-Phos catalyst system. Various diboron compounds could be used in this polymerization, and the obtained cross-conjugated polymers **P1**–**P3** were easily be converted into the linear-conjugated polymers **DP1**–**DP4** through a Diels–Alder reaction. We succeeded in changing the optical properties of **P1**–**P3**, such that, the maximum emission peaks in the fluorescence spectra of the linear-conjugated polymers **DP1**–**DP4** showed large redshifts compared to those of the cross-conjugated polymers **P1**–**P3**. Cross-conjugated polymers obtained by our method have the potential to be transformed into a variety of functionalized polymers including conjugated polymers. Additional investigations, including the synthesis of conjugated polymers from other dienophiles, are now in progress.

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